

AUTOENCAPSULATION: A NEW METHOD FOR ENTRAPPING PESTICIDES WITHIN STARCH

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A simple method to entrap pesticides under mild conditions is described. Pesticide is mixed with pregelatinized starch or ungelatinized starch containing a gelatinizing agent and enough water is added to allow agglomeration into 12- to 40-mesh granules. At this stage, much of the pesticide is not entrapped but is held firmly enough by the granules for handling. When the granules become wet, they also become gelatinous and then on drying form a solid matrix encapsulating the pesticide. Several pesticides were encapsulated by this method, and the encapsulation efficiencies for encapsulated products were determined.

INTRODUCTION

Controlled-release pesticide systems based upon entrapment in natural polymer matrices [1-3] are finding wide applicability because they reduce dermal toxicity [4], decrease environmental pollution due to reduced evaporative and degradative losses [5], give more effective control than conventional pesticide formulations over a longer time [6, 7], and are biodegradable [8]. These systems are relatively simple to formulate and do not require chemical modification of an existing pesticide.

At this laboratory, we have focused upon starch as the entrapping matrix because of its

film-forming properties, abundance, and low cost. Initially we reported a process to encapsulate pesticides with starch xanthate [9-12]. In this process, pesticide was dispersed in the xanthate and the xanthate was subsequently crosslinked either with an oxidizing agent such as hydrogen peroxide or a metallic salt such as ferric chloride. The crosslinking readily coagulated the product, which could then be easily filtered and dried to afford a granular material with sequestered pesticide.

Although the xanthate system gave products with controlled-release properties, the use of flammable and toxic carbon disulfide in preparing the xanthate and the instability of starch xanthate led us to develop alternate starch-based, controlled-release systems. One of these alternatives involved a starch-calcium adduct, where an alkaline starch-pesticide dispersion was coagulated with calcium chloride [13] and filtration followed by drying gave a highly alkaline granular product. Natural polymer matrices for entrapping pesticides were also made

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by reacting dispersions of pesticides and sodium alginate with calcium chloride or other salts [14, 15].

Another starch-based system involved coagulation of an alkaline starch-pesticide dispersion with boric acid [16, 17] to form an adduct which could be made into a granular material without using filtration. A mildly alkaline product was produced.

Others have reported that various degraded starches effectively entrap xanthophyll oil and Vitamin A [18] or essential oils [19]. These systems were made under neutral pH conditions and involve no chemical treatments that might adversely affect labile ingredients.

Because the above-described systems involve many steps such as mixing, shearing, filtering, grinding, and drying which can add appreciable processing costs to relatively inexpensive starting materials, a system is desired where the energy input of many steps could be reduced by having the entrapment take place during or after application to the field rather than prior to use. Such a concept is reported with the use of Carbozet[®] resins for "in flight" encapsulation [20].

We now report a process for encapsulations based on starch that involves fewer steps than our earlier methods, and where encapsulation occurs after the product is applied to the field. We have called this process "autoencapsulation" because the pesticide is encapsulated when the field-applied starch/pesticide granules are exposed to water and dry.

MATERIALS AND METHODS

Materials used for encapsulation including pearl cornstarch (CPC International, Englewood Cliffs, N.J.), Miragel 463[®] (A.E. Staley Mfg. Co., Decatur, Ill.), pregelatinized corn flour (Illinois Cereal Mills, Paris, Ill.), and poly(vinyl alcohol) as Elvanol[®] 52-22 (E.I. Dupont de Nemours Corp., Wilmington, Del.) were commercial grades. Pesticides used were

technical, emulsifiable concentrate, liquid, or wettable powder forms.

Trifluralin, an herbicide, was used to develop procedures for autoencapsulation because it is easy to extract from the product and to quantify. Samples containing starch and trifluralin (100 mg) were washed with chloroform to remove trifluralin adhering to the surface of the product. The washed product was then digested on a steam bath for 5 min in the presence of 2 *N* HCl (10 ml) to release the encapsulated trifluralin. Next the digest was cooled and extracted with chloroform. All chloroform solutions were diluted to 50 or 100 ml for the spectrophotometric quantification of trifluralin at 400 nm.

The matrix material used for encapsulation was brought into intimate contact with the trifluralin by techniques such as grinding, melting, mixing, or solvent dissolution and evaporation. The particle size of this matrix was next increased in size (12- to 40-mesh/400 to 1,700 μm) by adding water and various gel-promoting substances. After drying for one hour, the mixture was placed on a plastic sheet and sprayed with an excess of water (20:1) and dried. The techniques are illustrated in the following examples:

a. Technical trifluralin (10 g) was mixed with pearl cornstarch (40 g) and warmed on a steam bath until the trifluralin was completely melted and had uniformly coated the starch. The mixture was transferred to a large mortar and mixed with water (28 ml) to form a moist powder. Ground sodium hydroxide (4 g) was stirred in portionwise until a uniform agglomeration of particles was achieved. The product was removed, sieved to collect a 20- to 40-mesh fraction, and dried. A portion (100 mg) was spread uniformly on a plastic sheet and sprayed with water (2 g) from a glass atomizer. After drying, the product was removed from the sheet with a razor blade for determination of encapsulation efficiency.

b. Pearl cornstarch (20 g) uniformly coated with trifluralin (5 g) as above was mixed thor-

oughly with ground potassium hydroxide (3 g) in a large mortar and ice (15 g) was added. Continued grinding and slow availability of water through the melting of the ice allowed a controlled granulation. Controlled granulation was also obtained by adding water portionwise or via atomization during mixing.

c. Trifluralin (10 g) was melted and uniformly mixed with pearl cornstarch (40 g), then ground urea (20 g) and water (24 ml) were added with continuous grinding.

d. Pearl cornstarch (45 g) was mixed rapidly with a solution of trifluralin (5 g) in isopropyl alcohol (15 ml) dispersed in a solution of sodium hydroxide (6 g) in water (25 ml). Granulation took place after a few minutes. The solvents were then evaporated from the product. Similar results were obtained when chloroform or methanol was used in place of isopropyl alcohol.

e. Pearl cornstarch (45 g) was converted to a pregelatinized granular form by suspending it in water (250 ml), treating with 6.6% w/v sodium hydroxide (100 ml), and adding ethyl alcohol (500 ml). The dried product was sieved to collect a 20- to 40-mesh fraction. This fraction (10 g) was uniformly coated with melted trifluralin (2 g).

f. Miragel[®] 463, a powdered, pregelatinized cornstarch (10 g), was mixed uniformly with a solution of trifluralin (1.2 g) in methyl alcohol (4 ml). Water (2.5 ml) was mixed in rapidly to form a granular product which was sieved to pass 14 mesh. After air drying, a 20- to 40-mesh (400 to 800 μ m) fraction was collected.

g. Pregelatinized corn flour (45 g) was uniformly mixed with a solution of trifluralin (6 g) in chloroform (25 ml). Granulation was achieved by mixing with water (25 ml). A 20- to 40-mesh fraction was isolated after evaporating the solvents.

h. Poly(vinyl alcohol) (Elvanol[®] 52-22; 10 g) and melted trifluralin (3 g) were mixed uniformly, cooled, then sieved to afford a 20- to 40-mesh fraction.

i. Fifteen commercial herbicides and insecti-

cides were encapsulated by using Miragel[®] in a methanol-water system or by using pearl cornstarch in a sodium hydroxide-water system, with or without organic solvents. Pesticide on the surface of the product was removed by washing it with chloroform or hexane. Encapsulated pesticides stable to acid (such as thiocarbamates and dinitroanilines) were quantified using spectrophotometry or gas-liquid chromatography after acid digestion and extraction with a suitable solvent. Other pesticides, such as organophosphates and alachlor, not amenable to this technique were determined by elemental analyses for sulfur, nitrogen, or chlorine.

Release into air: Samples containing trifluralin (0.5 g) in 9 cm Petri dishes were exposed to an air flow of 200 ft/min under a hood for one month. Samples (50 mg) were analyzed periodically for total trifluralin using the indicated acid digestion and spectrophotometric quantification.

RESULTS

Pesticides were encapsulated by formation of a suitable composite of pesticide and starch (native or pregelatinized) which was subsequently sprayed with water and dried. If the composite contains starch in its native or ungelatinized form, the composite must be made with an adjuvant such as alkali or urea to promote gelatinization. The amount of adjuvant must be sufficient to gelatinize the starch in the presence of pesticide upon spraying with water. If the composite contains pregelatinized starch no adjuvant is necessary. Other substances such as certain grades of poly(vinyl alcohol) encapsulated pesticides successfully without adjuvants.

The initial composite is formulated preferably in the 12- to 40-mesh (400 to 1,700 μ m) range, the particle size typically used for granular pesticides. This range is achieved by regu-

lating mixing conditions and amount of water. A slow and uniform penetration of water into the composite is essential for uniform aggregation to produce the desired particle size. Such penetration can be achieved through the slow melting of ice, by the partitioning of the aqueous phase with organic solvents, or by alternate mixing and grinding operations. Sieving and drying should be done as rapidly as possible to prevent reaggregation or loss of volatile material. Commercial poly(vinyl alcohol) and laboratory samples of pregelatinized starches prepared by ethanol precipitation are often coarse enough to obtain 20- to 40-mesh fractions. Such samples may be coated with pesticide without using water or aqueous adjuvants prior to spraying.

The efficiency of encapsulation of the herbicide trifluralin in various autoencapsulating systems is shown in Table 1. It is seen that conditions can be chosen in most of these systems so that the initial composite may have less than 1/4th of the trifluralin encapsulated and the final composite after spraying and drying has over

3/4th encapsulated. The effect is seen most vividly where composites of trifluralin and pregelatinized starch or poly(vinyl alcohol), containing nearly all of the trifluralin on the surface, become 50 to 75% encapsulated after spraying and drying. The unencapsulated 25 to 50% remaining on the surface is moderately volatile, but if the sprayed product is dried and weighed within two hours a good material balance (over 90% recovery) of the starting trifluralin is obtained.

Release data obtained by exposing samples to the air over one month indicated that the initial composite lost trifluralin much more rapidly than composites that had been sprayed and dried. The example in Table 1 using pearl starch in an aqueous NaOH/CHCl₃ partitioned system gave an initial composite with 11% trifluralin encapsulated and 89% on the surface. One month's air exposure of this composite showed 57% loss of trifluralin. The composite obtained after spraying and drying showed 78% trifluralin encapsulated and 22% on the surface. One

TABLE 1

Autoencapsulating procedures of trifluralin^a

Wall material	Adjuvant	Solvent	% a.i. ^b	% Encapsulated ^c	
				initial	sprayed
PVA Elvanol [®] 52-22	none	none	23.1	2	52
Miragel [®] 463	none	H ₂ O/MeOH	10.7	10	78
Pearl starch	NaOH	water	16.6	24	81
	NaOH	water(ice)	18.5	32	79
	KOH	water(ice)	17.9	32	74
	NaOH	H ₂ O/CHCl ₃	10.5	11	78
	NaOH	H ₂ O/iPrOH	8.9	12	86
	urea	H ₂ O	14.3	31	68
Waxy maize	NaOH	H ₂ O	18.5	46	70
Pregelatinized cornstarch	none	none	16.7	1	76
Soft wheat flour	NaOH	H ₂ O/CHCl ₃	10.5	36	93
Soft wheat flour	urea	H ₂ O/CHCl ₃	7.9	27	47
Pregelatinized corn flour	none	H ₂ O/CHCl ₃	11.8	1	33

^aMesh range of particle sizes was 20-40 (400-800 μ m).

^bActive ingredient.

^cFreshly prepared samples.

TABLE 2

Autoencapsulation of pesticides and organic compounds

Compound	Common name	Anal. ^a	Proc. ^b	%a.i.	Mesh range	%Encapsulated	
						initial	sprayed
Acephate	Orthene [®]	S	A	9.1	14-20	85	94
Alachlor	Lasso [®]	UV	B	8.5	20-40	31	83
Atrazine	Aatrex [®]	N	B	8.2	20-40	25	87
		N	C	8.9	12-35	61	97
Butylate	Sutan [®]	N	B	8.9	20-40	29	95 ^c
		N	C	10.0	14-40	37	72 ^c
Chloramben	Amiben acid	N	A	11.2	14-20	86	100
Chlordane		Cl	A	10.0	14-20	78	94
Chlorpyrifos	(tech.)	Cl	A	7.5	14-20	73	87
	Lorsban [®]	Cl	A	8.9	14-20	25	53
Cyanazine	Bladex [®]	N	C	5.9	12-35	41	56
Diazinon	8 E	N	B	7.5	20-40	14	91
Eugenol		GLC	A	19.6	14-20	74	86 ^c
Gamma-HCH	Lindane [®]	Cl	A	6.4	14-20	14	63 ^c
Molinate	Ordram [®]	GLC	A	12.7	14-20	61	72 ^c
Oryzalin	Surflan [®]	VIS	B	9.3	20-40	26	74
Permethrin	Pounce [®]	Cl	A	8.9	14-20	24	100
Trifluralin	Treflan [®]	VIS	B	9.4	14-20	35	73

^aS, sulfur; N, nitrogen; Cl, chlorine; GLC, gas-liquid chromatography; VIS, visible spectroscopy; UV, ultraviolet spectroscopy.^bProcedure A: Compound (2-8 g), Miragel[®] 463 (20 g), methyl alcohol (15 ml), and water (10 ml). Procedure B: Compound (6 g), pearl cornstarch (45 g), sodium hydroxide solution (6 g in 25 ml of water) and chloroform (25 ml). Procedure C: Compound (6 g), pearl cornstarch (45 g) and sodium hydroxide solution (6 g in 25 ml of water).^cThese compounds lose 10-50% a.i. during the drying stages.

month's air exposure of this composite showed only 16% loss of trifluralin.

Autoencapsulating systems for various other pesticides and organic compounds are shown in Table 2. In some of these systems encapsulation was appreciable even before spraying.

Water-sprayed and dried products containing trifluralin that were washed with chloroform showed a slow release of trifluralin into this solvent. This effect was not observed in products of the xanthate, calcium or borate procedures containing trifluralin.

During 1985 field trials at Purdue University Agronomy Farm, an autoencapsulated product made from trifluralin, pearl starch, and potassium hydroxide gave significant reductions of giant foxtail stands and significant increases in crop yields when applied at the rate of 1.4 kg

a.i./ha 53 days prior to no-till planting of soybeans [21]. The product was comparable in performance to borate-encapsulated trifluralin and better than trifluralin in the form of Treflan[®] EC at comparable application densities. Yield increases observed in 1985 were confirmed in 1986 field trials.

DISCUSSION

The success of pesticide formulations of these types is based upon the presumption that there will be sufficient moisture under field conditions to "autoencapsulate" the active ingredient so that most of it will become encapsulated for prolonged controlled release. Preliminary field trials have shown such formulations to be

comparable in activity to borate-encapsulated formulations.

A wide variety of preparative conditions may be used to make formulations of this type. Pesticides labile under alkaline or acidic conditions may be formulated under neutral conditions using systems such as pregelatinized starch and water or native starch with aqueous urea as adjuvant. Much less water is used than in earlier starch-based encapsulating systems, which should lower processing costs. In many instances, such as where various commercial particulate pregelatinized starches and flours are used, it is possible to formulate such systems without water.

Water for field conditions may be supplied by rainfall, nocturnal condensation, or irrigation. Such systems should work well under no-till conditions where ground cover is available to retain soil moisture.

Observations of these systems during and after spraying suggest that encapsulation is most successful where there is a noticeable hydration and partial dissolution of the starch in the particles followed by formation of a hard, smooth, surface upon drying. Spraying with water onto relatively large plastic sheets allowed the particles to be separated far enough apart so that particles did not stick together during and after spraying. The slow release of pesticide into organic solvents from composites that had been sprayed and dried suggests a relatively more open structure not present in earlier [9-13, 16, 17] starch-encapsulated systems. Although evaporative losses of the initial composites can be considerable, such formulations do not lose appreciable pesticide upon air exposure once they have been suitably treated with water and dried.

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